Measurement of Surface Tensions of Surfactant Solutions[1]

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INTRODUCTION

In a study of the adsorption of sodium salts of α-sulfo-fatty acid esters at the water/vapor interface, it was necessary to determine the reliability of methods of surface tension determination. There are very few comparisons of methods in the literature (1, 2), especially for surfactant solutions. The first method tried was that of du Noüy. Reproducible values could not be obtained with solutions of surfactants, possibly because the surface was disrupted by detachment of the ring during measurement (1), and so the Wilhelmy plate and drop volume methods were investigated. Both of these methods were found to be satisfactory as discussed below. A further check was made using the pendant drop method, although the apparatus did not give very precise surface tension values.

The chief interest was in obtaining the amount of surfactant adsorbed Γ in the region of saturation adsorption (3), by application of the Gibbs equation in the form:

$$d\gamma = -RT\Gamma d(\ln c),$$

where c is the molarity of surfactant ions in aqueous solutions at constant concentration of sodium ions.

Saturation adsorption occurs in a concentration region below the cmc and is characterized by a linear portion in plots of γ against $\ln c$. To obtain the amount of surfactant adsorbed, the slope $d\gamma/d(\ln c)$ is re-

quired, so that absolute values of surface tensions are not as important as an acceptable degree of precision. A check was made of the accuracy of surface tension values obtained by the Wilhelmy plate and drop volume methods by comparing surface tensions of aqueous solutions of sodium chloride over the range 0 to 2 molar.

EXPERIMENTAL PROCEDURE

A. MATERIALS

Sodium hexyl α-sulfopelargonate (C_7H_{15}-CH(SO$_3$Na)COOC$_6H_{13}$; abbrev. NaHex-αSPelar, molecular weight 344.4) was prepared by Stirton et al. (4) and purified by extraction with toluene, then recrystallized from ethanol and dried under vacuum.

Sodium chloride, Baker Analyzed grade, was heated to 750°C. for 3 hours in a platinum crucible to remove surface-active impurities.

Triply distilled water was used to make up the solutions. The first distillation was from a block tin still. The second distillation was of dilute alkaline potassium permanganate solution from Pyrex glass. The water was then distilled through a well-leached Pyrex apparatus. The surface tension by the drop volume method was 72.00 $\pm$ 0.05 dynes/cm. at 25°C. (cf. I.C.T. value of 71.97 $\pm$ 0.05 dynes/cm.). The conductivity of the water in equilibrium with the atmosphere was approximately 1.1×10^{-6} mhos/cm.

B. METHODS OF SURFACE TENSION DETERMINATION

1) Wilhelmy Plate. With the Wilhelmy plate method, an analytical chainomatic balance was used. One of the pans was re-

placed by a silver chain hanging through a hole in the base into an air thermostat. Temperature control was to better than 0.1°C.

A sand-blasted platinum plate of perimeter 71.26 mm. was fastened to the chain. The plate was cleaned in hot chromic acid, rinsed with phosphoric acid, then with distilled water, and dried in a stream of nitrogen. By heating the plate to redness, which is often recommended for du Noüy rings, the degree of wetting of the plate was reduced, and therefore this step was abandoned.

Surface tensions were computed from the difference in weight between the dry plate and the plate with its lower end in a plane corresponding with the interface, according to the procedure of Ruyssen (5). The plate was not detached from the surface during measurement. The sensitivity of the balance allowed differences in surface tension of less than 0.02 dyne/cm. to be detected. The accuracy, governed by the uncertainty of 0.2% on the perimeter of the plate, is approximately ±0.07 when $\gamma = 30$ dynes/cm. and ±0.15 when $\gamma = 70$ dynes/cm.

2) Drop Volume. The drop volume apparatus was of simple design based on that of Gaddum (6), as described by Adam (7), except that there was no refilling attachment. Solutions were delivered from an Agla syringe through the cut-off end of a pipet (tip radius 1.371 mm.) which was ground flat on a fine carborundum stone. Drops were collected in a U tube which together with the barrel of the syringe was immersed in a water-bath thermostat maintained at 25° ± 0.01°C. The first three drops were neglected, and the mean of about ten successive drops was used to compute the surface tension using the correction factors of Harkins and Brown (8).

3) Pendant Drop. The pendant drop method was used as an additional check of the reliability of surface tension values obtained using the Wilhelmy plate and drop volume methods. The apparatus was similar to that used by Andreas, Hauser, and Tucker (9), but was not as precise partly because white light was used. The image of a drop was photographed and the negative enlarged so that drop dimensions could be obtained from a positive print. The boundary between drop and background on a print was not very sharp, and this contributed to the lack of precision. Surface tensions were calculated according to the method of Andreas, Hauser, and Tucker (9), but by using the tables of Fordham (10) and Stauffer (11).

RESULTS AND DISCUSSION

A. WATER AND SOLUTIONS OF SODIUM CHLORIDE

The surface tension values of 72.00 ± 0.05 dynes/cm. obtained by the drop volume method and 71.84 ± 0.20 dynes/cm. obtained by the Wilhelmy plate method for water at 25°C. are in good agreement with the generally accepted I.C.T. (12) value of 71.97 ± 0.05 dynes/cm., and with more recent values, for example, 71.98 ± 0.01 by Parreira (13) using drop volume, and 71.89 dynes/cm. obtained by Ruyssen (5) using the Wilhelmy plate method.

The surface tensions of sodium chloride solutions as a function of concentration are compared in Fig. 1. The difference between values obtained by drop volume and Wilhelmy plate methods is about 0.25 dynes/cm. and can be accounted for in terms of the uncertainty attached to the perimeter of the plate and the radius of the tip. Surface tension values from the I.C.T., interpolated to correspond to 25°C., are also included in Fig. 1 (the difference between molarity and molality—as quoted in I.C.T.—has been neglected). There is very good agreement between the I.C.T. values and those obtained by the drop volume method.

B. SOLUTIONS OF SODIUM HEXYL α-SULFOPELARGONATE

Surface tensions of solutions of NaHex-αSPelar in 0.01N sodium ion concentration obtained using the drop volume and Wilhelmy plate methods are presented as against ln c plots in Fig. 2, together with values obtained using the less precise pendant drop apparatus. The drop volume and Wilhelmy plate methods give straight lines in the range of saturation adsorption. The best line through the points from Wilhelmy plate is 0.5 dynes/cm. above that for drop volume, but the lines are parallel. Application of the Gibbs equation to the data gives a cross-
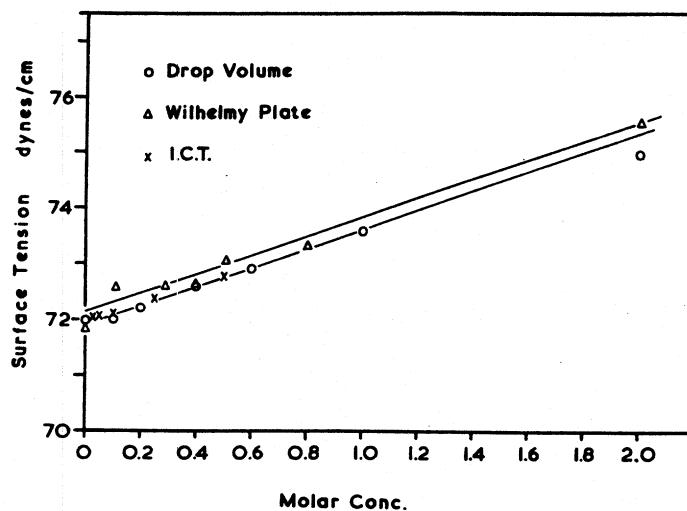
Fig. 1. Surface tensions of aqueous solutions of sodium chloride as a function of concentration at 25°C, obtained by drop volume and Wilhelmy plate methods, and including I. C. T. values.
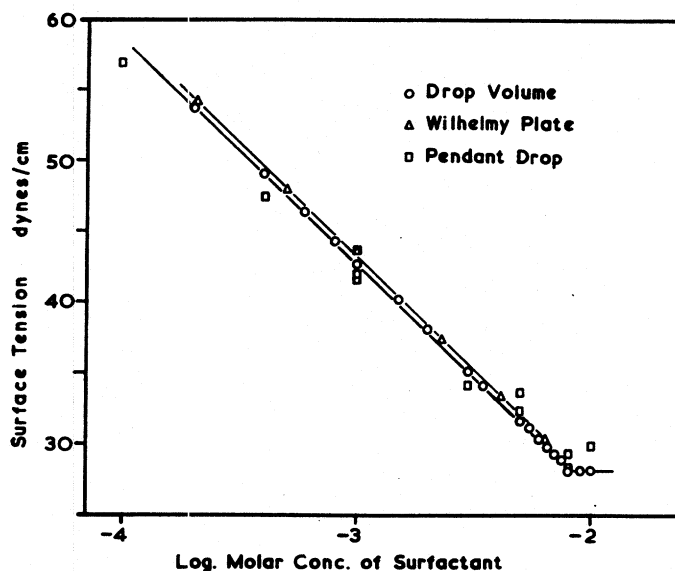

Fig. 2. Plots of surface tension against ln molar concentration for aqueous solutions of sodium hexyl α-sulfopelargonate at 25°C, obtained by drop volume, Wilhelmy plate, and pendant drop methods.

sectional area per molecule of NaHexαSPelar of 59 A² (cf. 53 A² obtained by Van Voorst Vader (3) for sodium dodecyl sulfate). The surface tension values obtained using the pendant drop method show considerable scatter but fall about the lines through the data from the other methods.

The area of 59 A² for a molecule of NaHexαSPelar is quite reasonable if the molecule is oriented normal to the water/air interface, and is comparable to the cross-sectional areas of other molecules of similar structure which have been investigated (14).

CONCLUSIONS

Both the Wilhelmy plate and the drop volume methods appear to be reliable for obtaining surface tensions of surfactant solu-

tions. There may, however, be slight systematic differences in actual values. The differences observed in this work are at most 1.5 %, and are much less than those found by Padday and Russell (1) for solutions of surfactants using the du Noüy method and a modified Wilhelmy plate method. The slight differences between values from the drop volume and the Wilhelmy plate methods found in this work do not affect molecular cross-sectional areas of surfactants as calculated from the Gibbs equation. The pendant drop method appears to give surface tensions in accord with those from the other two methods, when the limitations of the apparatus used are considered.

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